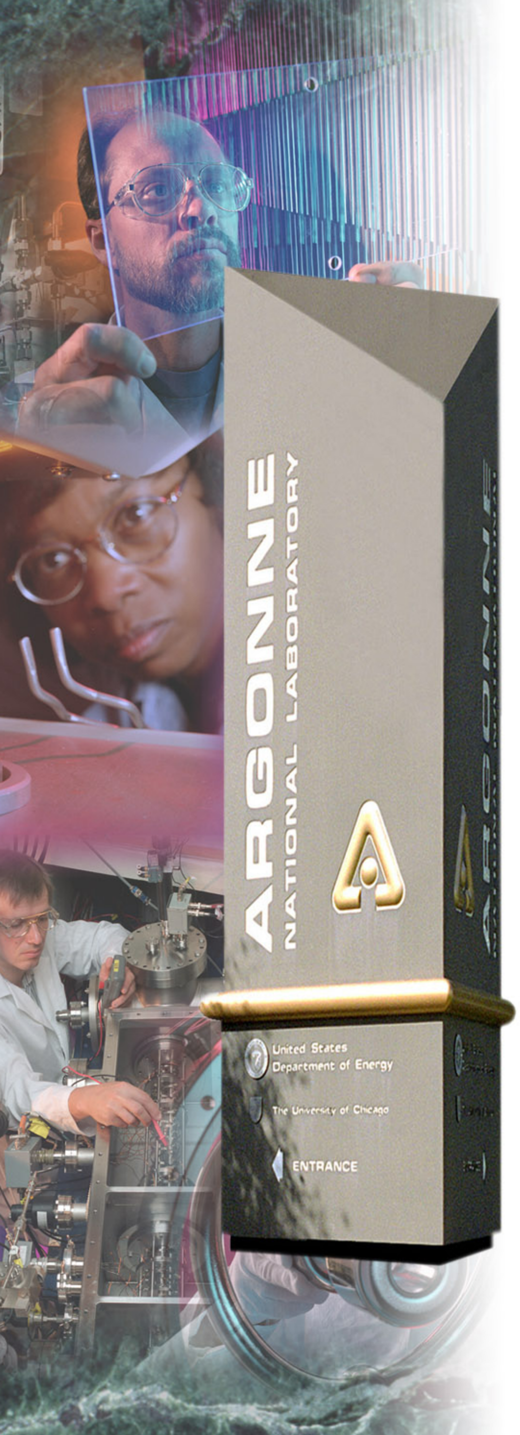


Alternative Thermochemical Cycle Evaluation

Michele Lewis
Argonne National Laboratory
May 23-26, 2005

This presentation does not contain any proprietary information

PD29

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Overview

Time Line

- Start date: 10/04
- End date: 9/05
- % complete: 40%

Barriers

- Unknown thermodynamic data
- Unknown chemistry

Budget

- FY 05 = $150K
- Complementary program supported by internal LDRD funds

Partners

- INERI with CEA
- INERI with AECL
- Primarily information exchange

Objectives/Deliverables

- **Review candidate alternative thermochemical cycles, characterize potential advantages and disadvantages**
- **Report – *Candidate Alternative Cycles for NHI Flowsheet Analysis* (2-1-05)**
- **Report - *Alternative Thermochemical Cycles for Nuclear Hydrogen Production* (9-1-05)**
  - Use updated assessments and downselect the most promising

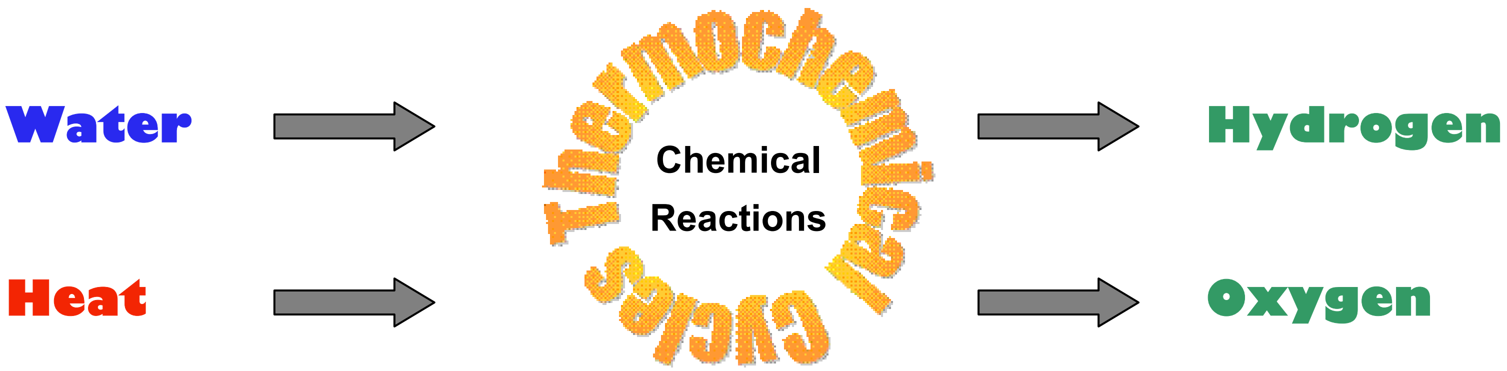
Other Objectives

- **Support two International Nuclear Energy Research Initiative (INERI) projects:**
  - Thermochemical Hydrogen Production Process Analysis (CEA)
    - *Collaborate on developing a standard, consistent methodology for quantifying cycle efficiency*
    - *Evaluate the S-I and an alternative cycle*
  - Lower-Temperature Thermochemical Hydrogen Production (AECL)
    - *Collaborate on assessing the use of lower-temperature cycles with nuclear reactor options*
      - Candu SCWR has an outlet temperature of 625C

Approach

- **Identify potentially promising cycles (2-1-05)**
  - Review literature, NE-R&D Plan, EERE programs, R&D at national labs and foreign research labs such as CEA
  - Determine benchmarks for assessing potential
    - *Reported idealized efficiencies*
    - *Reported evaluations of chemical viability*
- **Coordinate process for downselecting most promising cycles**
  - Perform scoping flowsheet analysis
  - Identify critical R&D needs for selected cycles
- **Select most promising cycles from updated assessments (9-1-05)**

Definition


Water
Heat
Thermochemical Cycles
Chemical
Reactions
Hydrogen
Oxygen

Literature Sources

- **Review articles that contain lists of cycles:**
  - Yalcin, Baumberger, Williams, Beghi (Ispra)
- **Individual papers within various journals:**
  - International Journal of Hydrogen Energy
  - Hydrogen Energy
  - Hydrogen Energy Progress
  - Alternate Energy Sources
  - More obscure journal articles by authors of interest

Literature Sources, Cont.

- **Two great summary reports available:**
  - GRI-80/0023.1 by McCarty, et al.
    - *Funded by The Gas Supply Research Division of the Gas Research Institute from 1972-1980*
    - *Contains efficiency and summary of experimental results*
    - *11 of 131 cycles selected as promising*
  - Solar Thermochemical Hydrogen Generation Report (STHGR) (to be published)
    - *Sponsored by DOE-EERE (Paster)*
    - *Contains a summary of 200+ cycles with efficiency for selected cycles*
    - *14 of 200+ cycles selected as promising*

Promising cycles from summary reports

- **GRI's Cycles**
  - Hybrid Cu-SO_4 (1100K)
  - Hybrid Cu-SO_4 (1363K)
  - Hybrid Zn-SO_4 (1150K)
  - Hybrid Cu-Cl (805K)
  - Hybrid Cd (1500K)
  - Cr-Cl (1475-1525K)
  - Fe-Cl (875-975K)
  - Fe-Cl (1175-1275)
  - NH_3-CO_3-Hg (875-975K)

- **STHGR's Cycles**
  - Cd-SO_4 (1475K)
  - BaMo-SO_4 (1275K)
  - Mn-SO_4 (1275K)
  - Hybrid Cu-Cl (825K)
  - Hybrid Cd (1475K)
  - Cd-CO_3 (1475K)
  - Multivalent sulfur (1845K)
  - Zn (2475K)
  - NiMnFe (1075K)
  - ZnMnFe (1475K)
  - NaMn-3 (1735K)
  - ?

Results: Rationale for Selection

- **Identify cycles with high idealized efficiency in both GRI and STHGR reports**

- **Eliminate cycles with maximum temperatures incompatible with the VTGR (<1150 K)**
  - Fe-Cl (875-975K)
  - NH_3-CO_3-Hg (875-975K)
  - Hybrid Cu-Cl (805K)
  - Hybrid Cu-SO_4 (1100K)
  - Hybrid Zn-SO_4 (1150K)
  - NiMnFe (1075K)

Results: Rationale for Selection-Cont.

- **Assess chemical viability**
  - Proof of principle work, if available
  - General chemical knowledge
    - *GRI provides useful experimental data for some cycles*
  - Cycles with Se, Hg, and Cd eliminated based on release rates for RICA metals

Results of literature search: 4 Cycles Selected

- **Hybrid metal sulfate, ‘proven’ chemistry:**
  - Cu: idealized efficiency of 69-73% (HHV); T_{max} = 1100 K
  - Zn: idealized efficiency of 55-61% (HHV); T_{max} = 1150 K
- **Hybrid Cu-Cl, ‘proven’ chemistry:**
  - Idealized efficiency = 49% (HHV); T_{max} = 805 K
- **Hybrid K-Bi cycle; general chemical knowledge:**
  - Idealized efficiency = 57% (HHV); T_{max} = 850 K

Other sources, other cycles?

- **Untapped sources**
  - Universities
  - Foreign institutions, companies such as GE, other national labs
- **Ongoing work is considered proprietary**
  - This presents a challenge in identification and assessment
- **Still open to new cycles**
  - Questions remain on Fe-Cl and on NiMnFe

Definitions

$$E = -\frac{\Delta H^\circ\left(H_2O(g)\right)(25^\circ\mathrm{C}))}{\Sigma Q}$$

- **Efficiency (LHV) with work inputs**

  - **- ΔH° (H2O(g)) = 57.8kcal/mol**
  - **$\Sigma Q = \Sigma q_i + \Sigma W_i/\eta$**
  - **W = the sum of the work inputs**
  - **η = efficiency of converting heat to electricity**

- **Electrochemical work from Faraday's law, $\Delta G = nFE$**
- **Energy for shaft work is based on typical engineering assumptions**

A Caution on Reported Efficiencies

- **Idealized efficiencies reported by various authors appear to use different assumptions**

	Efficiency from GRI (HHV)	Efficiency from STHGR (HHV)
Fe-Cl	47 – 49%	20%
Hy-S	41.5 – 49.2%	51%

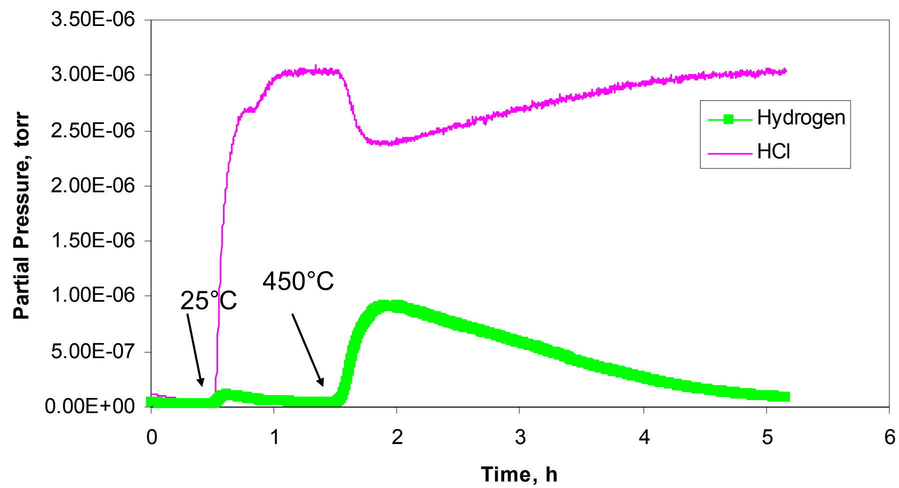
A Caution on Reported Efficiencies-Cont.

- **Unknown thermodynamic data**
  - No thermodynamic available for Cu_2Cl_2O
  - Incomplete thermodynamic data for HI-I_2-H_2O ternary
- **Inconsistencies in various thermodynamic databases**
- **Unknown assumptions in idealized efficiency calculations**
- **Unknowns in assessing chemical viability**
  - Yields, kinetics, separations, separation techniques, and amount of water in cycle
    - *Water removal is energy intensive*
  - Viability of reverse Deacon reaction-$Cl_2 + H_2O = 2HCl(g) + ½O_2$

Kinetics vs. thermodynamics

- **Realizable thermodynamics: necessary but not sufficient**

Temp., C	(ΔG), kcal/mol
25	-11.8
425	-0.5



- **Kinetics trumps thermo at 25C**

Ongoing Work - FY2005

- **Perform scoping flowsheet analyses on promising alternative cycles**
  - Make assumptions transparent
    - *Unknown thermodynamic data specified and estimation method clearly defined*
  - Use Excel format for new users (if possible)
  - Compare with other reported analyses
- **Develop critical guidelines for assessing chemical viability and identify most critical R&D needs for 4 cycles selected and provide guidance for new cycles**
- **Identify 'best' alternative cycles**

Possible guidelines for assessing chemical viability

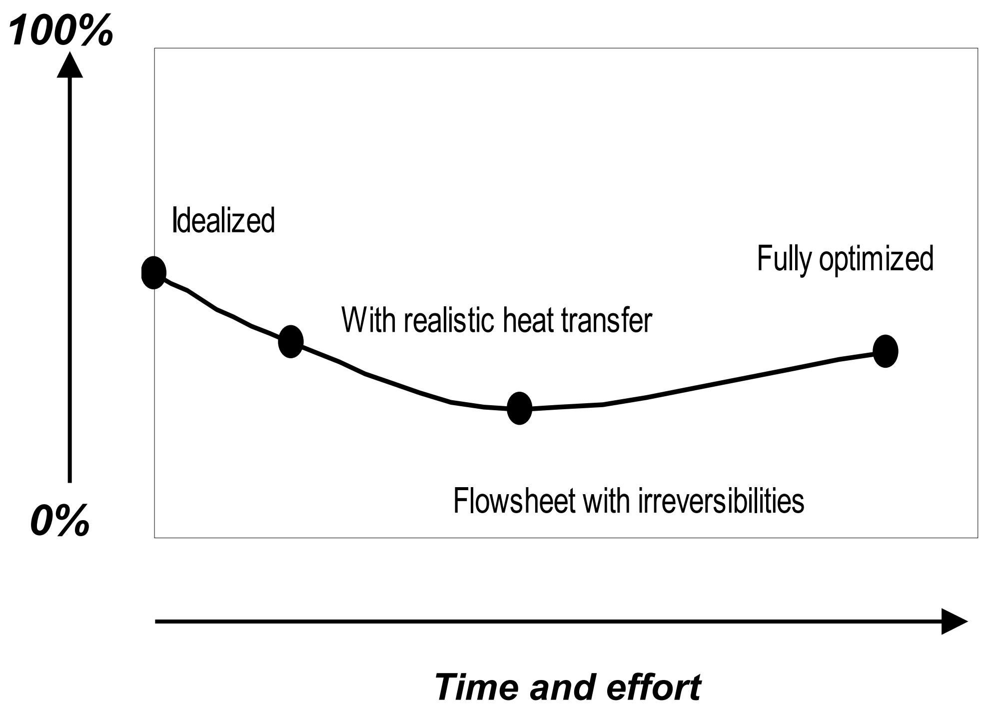
- **When proof of principle is absent**
- **Check spontaneity (ΔG) of reactions**
  - Check ΔG for each reaction: < $\pm$ 10-15 kcal/mol
    - *ΔG > -15 kcal/mol implies a very stable product*
    - *ΔG < +15 kcal/mol implies a reaction that does not go*
- **Check abundance and cost**
  - Cycles with Hg, Se, and Cd eliminated on the basis of EPA release rates for RCRA wastes; Ag cycles, on cost basis
- **Check number of elements and reactions**
  - No more than 2 other than O, and H
  - Relatively small number of reactions; how to define?

ANL-CEA Collaboration

- **Objectives of ANL-CEA INERI**
  - Develop a standard method for assessing thermochemical hydrogen production cycle efficiencies
  - Use methodology to compare leading technologies

- **Information exchange meeting**
  - ANL meeting on Feb. 3 and 4, 2005, with Pascal Anziew, Jean-Marc Borgard, and Philippe Carles of CEA
  - Agreed on general approach and noted that efficiency values change with knowledge of cycle
    - *CEA to define various levels of knowledge in cycle development*

High idealized efficiencies are necessary but not sufficient for assessment



Graph from CEA (Pascal Anziew)

Future Work: ANL/CEA Collaboration

- **Critical review of the NHI scoping methodology**
- **Define levels of cycle development and appropriate methodologies for calculating efficiency**
  - Different methods required for different levels of chemical and engineering knowledge
- **Define common parameters for simulations**
  - Engineering parameters
  - Guidelines for common unit operations for all thermochemical cycles
- **Joint authorship of several proposed papers**

Future Work: ANL/CEA Collaborations

- **Quantify Go/No-Go Criteria (part of chemical viability assessment)**
  - Consider cost/availability of raw materials at required level of purity
  - Assess environmental impact based on probable release rates
  - Determine impact of competing reactions
  - Determine consensus on maximum number of elements and maximum number of reactions
- **Energy usage optimization**
  - Balance process heat needs with heat source
  - Determine impact of transients
  - Determine effect of cogeneration

Future Work-ANL/AECL Collaborations

- **Collaborate on assessing the use of lower-temperature cycles with nuclear reactor options**
- **With funding**
  - Development of electrochemical cell for hybrid Cu-Cl cycle
  - An integrated demonstration by 2007
  - An economic assessment

Summary

- **Selected 4 cycles as promising alternative cycles for nuclear hydrogen production but still open**
- **Ongoing work includes scoping flowsheet analysis and identification of critical R&D needs**
  - Identify the most challenging reaction in a cycle
    - *Measurement of thermodynamic data, kinetic studies, proof of principle for reactions with high ΔG, determination of amount of water, or challenges in electrochemical cell configuration such as electrode material, catalysts, etc.*
- **Select most promising alternative cycles by 9-05**